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APPLICATION NUMBER: *60/480,348*
FILING DATE: *June 20, 2003*
RELATED PCT APPLICATION NUMBER: *PCT/US04/19769*

By Authority of the
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PTO/SB/16 (05-03)
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PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

Express Mail Label No. EL812538845US

Given Name (first and middle [if any])	Family Name or Surname	Residence (City and either State or Foreign Country)
James M.	Tour	Bellaire, TX

Additional inventors are being named on the 1 *separately numbered sheets attached hereto*

TITLE OF THE INVENTION (500 characters max)

POLYMERIZATION INITIATED AT THE SIDEWALLS OF CARBON NANOTUBES

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ENCLOSED APPLICATION PARTS *(check all that apply)*

☑ Specification *Number of Pages* 4
☑ Drawing(s) *Number of Sheets* 1
☐ Application Data Sheet. See 37 CFR 1.76
☐ CD(s), Number
☑ Other (specify) POSTCARD; CHECK

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☑ Applicant claims small entity status. See 37 CFR 1.27.
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The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.

☐ No.
☑ Yes, the name of the U.S. Government agency and the Government contract number are: NASA-URETI R75937-416000*, NASA-JSC-NCC-9-77, NSF/NSR-DMR-0073046 AFOSR/F49620-01-1-0364

[Page 1 of 2]

Respectfully submitted,

SIGNATURE Hugh R. Kress
TYPED or PRINTED NAME Hugh R. Kress
TELEPHONE 713-650-2714

Date 06/20/03
REGISTRATION NO. *(If appropriate)* 36,574
Docket Number: 11321/P068V1

USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT

This collection of information is required by 37 CFR 1.51. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 8 hours to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Mail Stop Provisional Application, Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

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PROVISIONAL APPLICATION COVER SHEET
Additional Page

PTO/SB/16 (05-03)
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Docket Number 11321-P068V1

INVENTOR(S)/APPLICANT(S)		
Given Name (first and middle [if any])	Family or Surname	Residence (City and either State or Foreign Country)
Jared L.	Hudson	Houston, TX

Number _____ of _____

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Polymerization Initiated at the Sidewalls of Carbon Nanotubes

Description of the invention:

The invention is a process for growing polymer chains via anionic, cationic or radical polymerization from the side walls of functional carbon nanotubes, which will facilitate greater dispersion in polymer matrices and greatly enhanced reinforcement ability in polymeric material.

Aryl bromide functionalized single wall carbon nanotubes (0.015 g, 0.022 mmol Br), (prepared according to Dyke, C. A.; Tour, J. M. "Solvent-Free Functionalization of Carbon Nanotubes," J. Am. Chem. Soc., 2003, 125, 1156 -1157 or Bahr, J. L.; Tour, J. M. "Highly Functionalized Carbon Nanotubes Using in Situ Generated Diazonium Compounds," Chem. Mater. 2001, 13, 3823-3824 or Bahr, J. L.; Yang, J.; Kosynkin, D. V.; Bronikowski, M. J.; Smalley, R. E.; Tour, J. M. "Functionalization of Carbon Nanotubes by Electrochemical Reduction of Aryl Diazonium Salts: A Bucky Paper Electrode," J. Am. Chem. Soc. 2001, 123, 6536-6542) are dispersed in THF (5 mL) and a solution of n-butyllithium (5 mL, 2.19 M in hexane) was added at 23 °C and the solution was allowed to stir for 10 min. The stirring was then turned off and the nanotubes were allowed to settle out of solution. After settling, the excess *n*-butyllithium solution was removed from the reaction vessel via cannula and the nanotubes were washed 3 times with dry THF (10 mL) remove traces of *n*-butyllithium. The flask was then charged with dry THF (10 mL) and the tubes were dispersed in solution with rapid stirring. Styrene (1.7 mL, 15 mmol) was added to the reaction vessel and the mixture was stirred for 180 min before adding ethanol (1 mL) or a function terminator of choice such as trimethylsilyl chloride. The mixture was then diluted with 100 mL dichloromethane and filtered through Fisherbrand P8 filter paper to remove any large particulate. The filtrate was concentrated under reduced pressure and precipitated into methanol. The resulting gray powder was then collected by filtration, using Whatman 41 filter paper and dried under vacuum (0.1 mm) to a constant weight (typically, 0.100-1.00 g depending on the precise amount of styrene added). This material can then be blended with other polymers or be molded and used by itself as a specialty material. (See attached Graphic)

The most immediate and obvious use of this invention is the improved dispersion ability in polymer matrices and the materials used by itself as a novel polymeric material that will offer enhanced strength and reinforcement ability when compared to its unbound polymer analog. Other applications involve attachment of any vinyl monomers via anionic, cationic or radical polymerization that can be extended into the realm of polyolefin and elastomer reinforcement etc.

No other method of polymerization initiated at the sidewalls of nanotubes has been shown to date.

The invention is a process involving the following steps:

1. Aryl bromide functionalized nanotubes are dispersed in a tetrahydrofuran solution of *n*-butyllithium.
2. The nanotube material is allowed to settle and the excess n-butyl lithium solution is removed via canulation.
3. The remaining nanotube material is washed with three portions of dry tetrahydrofuran to thoroughly remove any residual n-butyl lithium
4. Nanotube material is dispersed in dry tetrahydrofuran
5. After dispersion styrene monomer is added to the reaction vessel
6. Upon completion of the polymerization the active chain ends are terminated with an appropriate terminating agent.
7. After termination the reaction mixture is diluted and filtered to remove any large particulate.
8. The filtrate is then concentrated under reduced pressure and precipitated into methanol.
9. The resultant grey powder is collected via filtration and dried under vacuum to a constant weight.
10. This material may then be used as is or blended with other matrices to obtain superior dispersion and reinforcement properties.
11. One could also affect cationic or radical polymerization off the tube surface in this way. The process is not limited to anionic polymerization since a broad array of functional groups could be generated from the aryl sidewalls—see the papers cited above.

One could also effect cationic or radical polymerization off the tube surface in this way. The process is not limited to anionic polymerization since a broad array of functional groups could be generated from the aryl sidewall—see the papers cited above. Monomer selection is also not limited to styrenes. Since the previously mentioned polymerization methods are possible any monomer that can be polymerized by these techniques is a feasible variation. A list of example monomers, that is in no way comprehensive, is listed below:

Styrene
Ethylene
Propylene
Vinyl Halides
Isobutylene
Acrylic Acid
Acrylates
Methyl Acrylates
Vinyl Acetate
Vinyl Pyridines
Isoprene
Butadiene
Chloroprene
Acrylonitrile
Maleic Anhydride

Grant or Contract Number:
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What is claimed is:

1. A method comprising:

a) providing aryl bromide functionalized carbon nanotubes;

b) dispersing said aryl bromide functionalized carbon nanotubes in a solvent;

c) adding an alkyllithium species to the solvent for initiating polymerization on the sidewalls of the carbon nanotubes;

d) adding a monomer to the solvent; and

e) adding a suitable function terminator.

2. The method of Claim 1, wherein the solvent is tetrahydrofuran.

3. The method of Claim 1, wherein the alkyllithium species is n-butyllithium.

4. The method of Claim 1, wherein the monomer is selected from the group consisting of styrene, ethylene, propylene, vinyl halides, isobutylene, acrylic acid, acrylates, methyl acrylates, vinyl acetate, vinyl pyridines, isoprene, butadiene, chloroprene, acrylonitrile, maleic anhydride, and combinations thereof.

5. The method of Claim 1, wherein the monomer is styrene.

6. The method of Claim 1, wherein the function terminator is selected from the group consisting of ethanol, trimethylsilyl chloride, and combinations thereof.

7. The method of Claim 1, wherein the function terminator is ethanol.

Process for Sidewall Initiated Polymerization